

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

1       IN RE: The application of James Robert Allen and Michael Katz

2                               **TITLE OF THE INVENTION**

3       Environmentally Safe Substitute For Lead Shot

4                               **CROSS REFERENCE TO RELATED APPLICATIONS**

5       Not Applicable

6                               **STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH AND**  
7                                               **DEVELOPMENT**

8       Not Applicable

9                               **BACKGROUND OF THE INVENTION**

10       Field of the invention

11       This invention relates to substitutes for lead shot tools and particularly to  
12 environmentally safe substitutes for lead shot.

13       2. Description of the Prior Art

14       Because the use of traditional lead (Pb) shot has been outlawed for waterfowl  
15 hunting in the U.S., Canada, UK and other countries, much effort has been devoted to  
16 identifying a suitable substitute. To be fully satisfactory, alternative shot must possess  
17 the following attributes:

18       a) The material should have density similar to that of lead (Pb) shot, typically  
19 11.0 g/cm<sup>3</sup>.

20       b) The material must not cause physiological problems in wildlife that may  
21 ingest spent shot from the ground or water.

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1 c) The material must not cause significant damage to shotgun barrels.

2 d) The shot must possess sufficient strength, rigidity and toughness to  
3 adequately withstand "set-back" forces associated with firing and to penetrate the target  
4 effectively without shattering or excessively deforming.

5 e) For purposes of game law enforcement, shot material should preferably be  
6 magnetic to easily differentiate it from illegal lead shot.

7 f) Material used for shot must be economical to obtain and fabricate into  
8 spherical product.

9 None of the alternative shot types currently available conforms to all of the  
10 above criteria. Current products in the USA include shot made of steel, bismuth alloy,  
11 iron-tungsten alloy and tungsten-polymer composite. Each of these will be reviewed  
12 and critiqued in the following discussion, followed by a review of other prior art, which  
13 has not yet become commercialized.

### 14 Steel Shot

15 The most widely used alternative shot is carbon steel, in spite of the fact that its  
16 density is quite low (about 7.9 g/cm.<sup>3</sup>) in comparison with that of lead shot (about 11.0  
17 g/cm<sup>3</sup>). Inarguable principles of physics and engineering establish that an object of  
18 lower density, when moving through a fluid (such as air), will carry less energy at any  
19 given velocity, and experience more rapid loss of velocity (due to drag forces) than an  
20 object of higher density of the same size and shape. Shot shell manufacturers have  
21 employed special powders to increase steel shot velocity, in an attempt to ameliorate its  
22 inferior ballistic properties. The "hotter" powders unfortunately create higher pressures

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1 within the gun barrel. Safety considerations have therefore prompted shot shell  
2 manufacturers to recommend that steel shells only be fired in certain types of modern,  
3 high-strength shotguns.

4 There is also a significant negative impact of steel shot on the very same wildlife,  
5 which the outlawing of lead is intended to preserve. The inferior ballistics of steel shot,  
6 in the hands of the public, has resulted in higher rates of "crippling" shots. This is  
7 because generations of hunters accustomed to shooting traditional lead shot tend to  
8 attempt to shoot waterfowl at the same distances that they have always considered to  
9 be "in range."

10 Another approach taken by steel shot shell manufacturers has been to simply  
11 substitute larger steel shot for traditional lead shot sizes, in order to provide equivalent  
12 mass. This practice has the obvious disadvantage that there are fewer shot in any given  
13 shell. The "pattern density" of the cloud of shot is lower at any given distance from the  
14 point of firing. This sparse pattern again increases the probability that birds will be  
15 crippled, rather than harvested for consumption.

16 Bismuth alloy shot shells (see e.g., U.S. Pat. No. 4,949,644 to Brown) are currently  
17 marketed in the USA at approximately three times the cost of steel shells.  
18 Unfortunately, bismuth alloys are not equivalent to lead in density (about 9.4 g/cm.<sup>3</sup> vs.  
19 11.0 g/cm.<sup>3</sup>), although somewhat more dense than steel (7.9 g/cm.<sup>3</sup>). In addition to this  
20 shortcoming, bismuth alloys are inherently brittle and therefore tend to fracture and  
21 disintegrate upon impact. As fracture surfaces form in the shot, energy is lost, which  
22 would otherwise be available to enhance penetration of the target. In this instance, it is

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1 even likely that all the increased energy gained by having higher density pellets than  
2 steel is lost as fracture occurs. Finally, it should be noted that bismuth is non-magnetic  
3 and cannot be readily distinguished from illegal lead shot by game officers in the field.

4 U.S. Patent Nos. 5,264,022, 5,527,376, and 5,713,981 disclose a more recent  
5 product, which began to be marketed in the USA in 1997. It is a shot shell containing  
6 binary iron-tungsten alloy shot (60%Fe-40%W, by weight). Because the Fe--W is very  
7 hard (about Rockwell C50), it must be ground with ceramic abrasives (alumina, silicon-  
8 carbide, diamond, etc.), particles of which become imbedded in the shot surface. As a  
9 result, this type of shot produces severe damage in all gun barrels unless the shot is  
10 encapsulated in a special "overlapping double-wall" plastic shot-cup of heavy  
11 construction. Even with this precautionary design, the manufacturer prints a clear  
12 message on each box of product disclaiming any responsibility for gun barrel damage  
13 or personal injury. The consequences of forming longitudinal scratches in the barrel  
14 caused by this shot are that stresses produced by the expanding explosive gases will be  
15 concentrated in the regions around the scratches. A primary concern is that these  
16 stresses may be sufficiently high to cause catastrophic bursting of the barrel.

17 Whether adequately protective or not, the special plastic shot-cup (or "wad")  
18 creates another significant problem. The wad must be made of plastic tubing so thick as  
19 to make it impossible to load quantities of shot equivalent to those of traditional lead  
20 shells. For example, Fe--W shells of 2-3/4-inch length for 12-gauge guns contain only  
21 1.0 ounce of shot versus 1-1/8 to 1-1/4 ounces in corresponding lead or steel shells. The  
22 deficient pellet numbers result in correspondingly sparse pattern densities, the same

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1 problem encountered in substituting larger steel shot for traditional lead sizes, as  
2 mentioned previously.

3 Although denser than bismuth shot, Fe--W shot currently marketed is still  
4 considerably less dense than lead shot (about 10.2-10.5 g/cm.<sup>3</sup> vs. 11.0 g/cm.<sup>3</sup>). When  
5 this fact is combined with the lower pattern densities, the purported advantages of Fe--  
6 W shot over steel shot become questionable.

7 Finally, problems associated with manufacturability, and their adverse effects on  
8 product cost, are relatively severe. The constituent phases in Fe--W alloys cause the  
9 shot to be so hard and brittle as to be impossible to forge or swage these alloys into  
10 rods, or even to shape them compressively into spheres. Although the referenced  
11 patents claim Fe--W shot can be made by casting, the inherent brittleness and high  
12 melting temperatures of these alloys caused cracking to occur during rapid cooling.  
13 Cracking also plagued the process of compressive grinding, which was tried as a means  
14 of rounding the generally asymmetrical shot. Consequently, the shot actually being  
15 produced and marketed must be made by an expensive powder metallurgical method.  
16 Even with this approach, only larger shot sizes ("BB" 0.180-inch-diameter, and "#2"  
17 0.150-inch-diameter) are being produced at present. This is because powder-processing  
18 costs increase exponentially as shot sizes decrease. Furthermore, the fragility of  
19 compaction tooling becomes a limiting factor as shot size decreases. Shot sizes #4  
20 (0.130-inch), #5 (0.120-inch), #6 (0.110-inch) and #7 1/2 (0.095-inch), traditionally  
21 preferred for hunting all but the very largest game birds (such as geese), are unavailable  
22 for these reasons.

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1 Attempts to increase Fe--W shot densities to be equivalent to lead shot are  
2 frustrated by the fact that elevating tungsten content not only raises material costs but  
3 further exacerbates manufacturing problems. As in the case of bismuth shot, Fe--W  
4 shells are about three times as expensive as steel shells, thereby rendering them  
5 unaffordable by the average sportsman. Unlike steel shot, which can be obtained by the  
6 average citizen to reload his own sporting ammunition, Fe--W shot and the special  
7 plastic wads, which make it safer to use have not been made available to the public for  
8 reloading.

9 A composite of tungsten powder and a powdered polymer is disclosed in U.S.  
10 Patent No. 4,949,645 to Hayward et al. This shot material is a composite of tungsten  
11 powder and a powdered polymer (e.g., nylon, polyethylene, et al). Mixtures of these  
12 two constituents are formed into spheres of cured composite, the polymer "glue" being  
13 the continuous phase, and the tungsten powder particles, the discontinuous phase. By  
14 virtue of its weak polymer-to-metal bonds, the material will reportedly not damage gun  
15 barrels. It is this very "weakness", however, which is one of the undesirable features of  
16 tungsten-polymer shot. Rigidity and strength are important material properties that  
17 affect the ability of shot to (1) penetrate the target effectively, and (2) remain spherical  
18 during launch and flight.

19 Because the elastic moduli of all organic polymers are far lower than those of  
20 metals, the subject composite materials are, as expected, less rigid than steel, Fe--W, et  
21 al. This results in degraded penetration. Moreover, this shot is also subject to  
22 permanent distortion, referred to as "plastic deformation, which results in a loss of

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1 sphericity. Any loss of sphericity results in erratic flight paths of shot and, therefore,  
2 produces undesirable pattern uniformity.

3 Another disadvantage of tungsten-polymer shot is one of economics. Because  
4 polymers are much lower in density than common metals such as iron, a composite  
5 density equivalent to that of lead shot ( $11.0 \text{ g/cm}^3$ ) can only be attained by using high  
6 concentrations (e.g., 95%) of costly tungsten powder.

7 As in the case of bismuth, tungsten-polymer shot is non-magnetic, making it  
8 difficult for law enforcement to distinguish it from illegal lead shot.

9 Alternative shot materials in this category are disclosed in U.S. Patent No.  
10 5,279,787 to Oltrogge, U.S. Patent No. 5,399,187 to Mravic et al, and U.S. Patent No.  
11 4,784,690 to Mullendore et al. As in the case of Fe--W shot, such processes at most can  
12 only be expected to be economically feasible for the larger shot sizes, which have  
13 limited usefulness.

14 Other proposed shot materials include significant concentrations of lead as a  
15 specified ingredient. Recent rulings by the U.S. Fish and Wildlife Service have  
16 outlawed the use of any shot material containing more than 1.0% lead. This action has  
17 eliminated consideration of proposed materials described in a variety of U.S. Patents:  
18 U.S. Patent Nos. 2,995,090 and 3,193,003 to Daubenspeck; 4,027,594 to Olin; 4,428,295 to  
19 Urs; 4,881,465 to Hooper; and 5,088,415 to Huffman et al are examples.

20 Even materials that are lower in density than steel have been proposed for  
21 alternative shot. Examples are zinc ( $7.14 \text{ g/cm}^3$ ) and tin ( $7.3 \text{ g/cm}^3$ ). Such materials  
22 certainly offer no improvement in ballistic properties over those of steel shot.

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### BRIEF DESCRIPTION OF THE INVENTION

The instant invention over comes these problems. It consists of a shot pellet that, in one embodiment, has an inner core of tungsten carbide that is coated with a layer of bismuth. This coating is molecularly bonded to the tungsten carbide and is not an alloy.

The instant invention addresses the disadvantages of the shot addressed above, while maintaining all advantages. The unique properties of the instant invention allow its density to be tailored. As explained in below, the effective density of the instant invention can be made to be identical to lead for direct replacement in current lead loading formulations. Additionally, the density can be made to be lower than lead for shotguns requiring low barrel pressures, or higher than lead for enhanced energy transfer while maintaining the other advantages of the instant invention.

### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a table showing a comparison of test-firings using a variety of prior art shot pellets and pellets of the instant invention.

### DETAILED DESCRIPTION OF THE INVENTION

The instant invention is a two-part shot that uses an inner core of Tungsten, or Tungsten Carbide, or Tungsten Iron. All of these materials have a density greater than that of lead. All are considered non-toxic by US EPA, and are approved for hunting on federal game lands. The inner core is then encased in an outer core of Bismuth, or Bismuth/Tin alloy. Both of these materials have a density less than that of lead. Both



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1 are considered non-toxic by US EPA and are approved for hunting on federal game  
2 lands.

3 In one embodiment, the invention uses an optional binding layer of Nickel. This  
4 material has a density less than that of lead, is considered non-toxic by US EPA, and is  
5 approved for hunting on federal game lands.

6 Additional materials having a density equal to or greater than lead and non-toxic  
7 can be used for the inner core. However, tungsten or tungsten carbide are preferred.

8 Additional materials having a density equal to or less than lead and non-toxic  
9 can be used for the outer core.

10 The weight of a sphere may be expressed in terms of both its density and its  
11 diameter. The equation for this calculation is:

12  
13 EQ1:  $W = (4/3) * \pi * r^3 * d$

14  
15 where r = Radius of sphere and d=density of material of construction

16 The weight of a sphere with an outer annulus of dissimilar material may also be  
17 expressed in terms of the density and diameter of both the inner and outer material.

18 The equation for this calculation is:

19  
20 EQ2:  $W = (4/3) * \pi * r_{inner}^3 * d_{inner} + (4/3) * \pi * r_{outer}^3 * d_{outer} - (4/3) * \pi * r_{inner}^3 * d_{outer}$

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Where  $r_{\text{inner}}$  = radius of inner material and  $d_{\text{inner}}$  = density of inner material of construction and  $r_{\text{outer}}$  = radius of outer material and  $d_{\text{outer}}$  = density of outer material of construction.

Equation 2 may be simplified to equation 3

$$\text{EQ3: } W = (4/3) * \pi * (r_{\text{inner}}^3 * d_{\text{inner}} + r_{\text{outer}}^3 * d_{\text{outer}} - r_{\text{inner}}^3 * d_{\text{outer}})$$

Where all the terms have been defined above

For the following examples, the following data is used:

11.3 g/cc Density Lead

8.90 g/cc Density Nickel

9.79 g/cc Density Bismuth

9.71 g/cc Density Bismuth/Tin

19.30 g/cc Density Tungsten

15.00 g/cc Density Tungsten Carbide

15.00 g/cc Density Tungsten Iron Alloy

Note that the final outer diameter may be varied to produce materials of virtually any diameter. The examples below will use standard shot sizing.

Methods of Manufacture

In the broadest sense, this invention produces a multilayered annular metallic composite where the finished product has an outer surface with the hardness and lubricity properties of lead and an inner core with enhanced density.

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1       The examples below describe preferred embodiments. Additional methods of  
2       manufacture similar to these methods, but not described below can be used with equal  
3       results.

4       In this embodiment, three methods of manufacture are disclosed. The first is the  
5       use of powder and punch press technology to produce a finished sphere. The second is  
6       the use of powder and pre-made core technology to produce a finished sphere. The  
7       third is the use of powder and punch press technology to produce a finished sphere of  
8       pure Bismuth tin.

9       The following examples illustrate these methods. Note that the size and  
10      densities of shot pellets produced in these examples are not limited. The size of shot  
11      shown is merely an example of the process. All sizes of shot can be made using any of  
12      these processes, within the limitations of the densities of the material. As discussed  
13      above, the densities can be set to be equal that of lead, or to be lighter or heavier, as  
14      desired.

### 15      Example 1

16      The use of powder and punch press technology to produce a finished sphere  
17      equivalent to # 8 shot at the exact equivalent density of lead using a core of tungsten.  
18      Note that the equivalent diameter of #8 shot is 2.29 mm. Tungsten powder (-200 mesh)  
19      is pressed in a punch press at 25 tons to form an inner core of 1.257 mm. This inner core  
20      is then cleaned to remove residual press oils. The resulting inner core is then inserted in  
21      a second press. This press uses the inner core and a quantity of bismuth/tin powder  
22      (-200 mesh), which is pressed at 23 tons to form a finished sphere of 2.29 mm. By using

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1 an inner core of 1.257 mm and a final sphere size of 2.29 mm, the effective density is  
2 exactly equivalent to that of lead, and the diameter is precisely that of # 8 shot with an  
3 approximate hardness equivalent to that of lead.

### 4 Example 2

5 The use of powder and pre-made core technology to produce a finished sphere  
6 equivalent to #7.5 shot at the equivalent density of a heavy shot (1.1 x density of lead)  
7 using a core of tungsten carbide. Note that the equivalent diameter of #7.5 shot is 2.41  
8 mm. A tungsten carbide core of 1.930 mm is selected as the inner core for this example.  
9 The core is cleaned and referred to below as the inner core. A punch press uses the  
10 inner core and a quantity of bismuth/tin powder (-200 mesh), which is pressed at 23  
11 tons to form a finished sphere of 2.41 mm. By using an inner core of 1.930 mm and a  
12 final sphere size of 2.41 mm, the effective density is exactly equivalent to that of 110% of  
13 lead, and the diameter is precisely that of # 7.5 shot. The bismuth/tin alloy has an  
14 approximate hardness equivalent to that of lead

### 15 Example 3

16 The use of powder and punch press technology to produce a finished sphere  
17 equivalent to #4 shot at any density below that of pure Bismuth tin using a core of  
18 mixed tungsten/bismuth. Note that the equivalent diameter of #4 shot is 3.30 mm. A  
19 blend of tungsten powder (-200 mesh) and 97/3 bismuth/Tin and is pressed in a punch  
20 press at 25 tons to form a inner core of 2.167 mm. This inner core is then cleaned to  
21 remove residual press oils. The inner core is placed in a punch press with a quantity of  
22 bismuth/tin powder (-200 mesh) and pressed at 23 tons to form a finished sphere of

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1 3.30 mm. For the case where the density of the finished shot equals that of bismuth tin  
2 (9.71 g/cc, or 86% of lead), the inner core is comprised of 100% bismuth tin. For the  
3 case where the density of the finished shot equals that of a heavy shot (12.43 g/cc, or  
4 110% of lead), the inner core is comprised entirely of tungsten, with an outer annulus of  
5 bismuth/tin. By using an inner core of 2.167 mm and a final sphere size of 3.30 mm, the  
6 effective density can be tailored by a simple stoichiometric ratio of inner material with  
7 the diameter precisely that of # 4 shot. The bismuth/tin alloy has an approximate  
8 hardness equivalent to that of lead.

9 An alternative method of manufacture involves the use of a continuous hollow  
10 wire of bismuth or, preferably, bismuth-tin. A tungsten core is then inserted into the  
11 center of the hollow wire. Preferably, the tungsten core is actually a slurry or tungsten  
12 power bound in a digestive wax. This mixture is then inserted into the wire. The result  
13 is a wire with a tungsten core and a covering of bismuth or bismuth-tin. This wire is  
14 then processed by segmenting it into small sections, which are then cut and punch  
15 pressed into individual spheres.

16 Figure 1 is a table showing a comparison of various forms of prior art shot and  
17 the shot made with the process discussed herein. The table shows the type of shot used  
18 and the loading specifications and the ballistic characteristics for each type of shot. The  
19 purpose of this table is to show the comparison of the lead shot alternatives to actual  
20 lead shot. As shown in the figure, a sample of the shot was made that compares  
21 directly to a number 7.5 lead shot. As expected, the difference between the lead shot  
22 and the shot of the instant invention was negligible. Thus, pellet for pellet, the

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1 characteristics of the shot of the instant invention are equal that of lead. Using the shot  
2 of the instant invention allows loading of shells using the same tables, charts, tools and  
3 equipment for loading lead shells.

4       The present disclosure should not be construed in any limited sense other than  
5 that limited by the scope of the claims having regard to the teachings herein and the  
6 prior art being apparent with the preferred form of the invention disclosed herein and  
7 which reveals details of structure of a preferred form necessary for a better  
8 understanding of the invention and may be subject to change by skilled persons within  
9 the scope of the invention without departing from the concept thereof.